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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Hiroshi NEMOTO, Michio TAKAHASHI and Kenshin KITO

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For: LITHIUM SECONDARY BATTERY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

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Janet M. Stevens
Janet M. Stevens

DECLARATION UNDER 37 CFR §1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Michio Takahashi, a citizen of Japan, hereby declare and state:

1. I have a master's degree in engineering which was conferred upon me by Waseda University in Tokyo, Japan, in 1991.
2. I have been employed by NGK INSULATORS, LTD. since 1991 and I have had a total of 7 years of work and research experience in the field of batteries, including lithium secondary batteries.

3. I am a co-inventor of the above-identified patent application and I am familiar with the references applied in the Office Action mailed on August 25, 2003.

4. My work in the field of batteries includes speaking on preparation of $\text{Li}_2\text{S-SiS}_2$ lithium ion conductive solid electrolyte before the 43rd Battery Symposium in Japan.

5. The following experiments were conducted by me or under my direct supervision.

As the starting raw material, commercially available Li_2CO_3 , MnO_2 , Co_3O_4 , TiO_2 , Al_2O_3 and GeO_2 powders were weighed and mixed so that the positive active material compositions of the respective examples (Example A, Example B, Example C and Example D) shown in Table 1 (positive active material compositions) can be obtained. The respective mixtures of powders were each fired at 800°C in an air atmosphere for 24 hours to obtain the positive active materials listed in Table 1.

In order to prepare coin cells, positive materials prepared by mixing each of the respective positive active materials with acetylene black powder as a conductive material and polyvinylidene fluoride as a bonding material in a ratio of 50 parts positive active material, 2 parts acetylene black powder and 3 parts polyvinylidene fluoride. Then, 0.02 grams of each positive material was pressed formed under a pressure of 300 kg/cm^2 in order to prepare disc shapes having diameter of $20\text{ mm } \phi$ to be used as the positive pole. Electrolyte was formed by dissolving LiPF_6 as an electrolyte into an organic solvent with ethylene carbonate and diethyl carbonate in equal volume ratios to provide a density of 1 mol/L . Negative poles were made of carbon. Coin cells were formed using the positive pole described above, the electrolyte described above, negative poles described above and separators separating the positive and negative poles.

In order to measure the respective internal resistance ratios, each of the respective coin cells was subjected to one cycle of charging and discharging, involving charging constant current of 1C rate and constant voltage of 4.1V in accordance with the capacity of the positive active material, and discharging constant current of 1C rate and constant voltage of 2.5V. In each case,

the respective battery's internal resistance was obtained by dividing the difference between the potential at a resting state after finishing charging and the potential immediately after commencement of discharging (potential difference) with discharged current. The internal resistances of the respective batteries were divided by the internal resistance of a battery using an original compound which did not undergo elemental substitution (i.e., LiMn_2O_4) to yield the internal resistance ratio. Accordingly, as the value of internal resistance ratio decreases, the reduction of internal resistance increases. The respective internal resistance ratios of the respective examples are each shown in Table 1.

[Table1]

	Positive active material composition	Internal resistance ratio of coin cells (%)
Example A	$\text{Li}(\text{Co}_{0.5}\text{Ti}_{0.5})_{0.01}\text{Mn}_{1.99}\text{O}_4$	96
Example B	$\text{Li}(\text{Co}_{0.5}\text{Ti}_{0.5})_{0.10}\text{Mn}_{1.90}\text{O}_4$	89
Example C	$\text{Li}(\text{Al}_{0.5}\text{Ge}_{0.5})_{0.07}\text{Mn}_{1.93}\text{O}_4$	103
Example D	$\text{Li}(\text{Al}_{0.5}\text{Ge}_{0.5})_{0.10}\text{Mn}_{1.90}\text{O}_4$	112
Ref.A(Embodiment6)	$\text{Li}(\text{Ni}_{0.5}\text{Ti}_{0.5})_{0.01}\text{Mn}_{1.99}\text{O}_4$	52
Ref.B(Embodiment7)	$\text{Li}(\text{Ni}_{0.5}\text{Ti}_{0.5})_{0.10}\text{Mn}_{1.90}\text{O}_4$	36

6. I have studied the results of the above-described examples, and compared them with results of tests described in the present specification, in particular, Embodiments 6 and 7 (specification, pages 22-29, results shown in Table 1 on page 24). Based on those comparisons, in which the internal resistance ratio of the coin cell of Embodiment 6 was 52% and the internal resistance ratio of the coin cell of Embodiment 7 was 36%, it is clear to me that Examples A, B, C and D reported herein showed higher internal resistance ratios than the coin cells of Embodiments 6 and 7 reported in the present specification. This difference in internal resistance ratio would have been completely unexpected to those of skill in the art, and this unexpected result indicates that a combination of nickel and titanium substituents of Mn in accordance with the present invention is superior to other combinations of substituents in reducing the internal resistance of cells.

7. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: December 24, 2003

Michio Takahashi
Michio Takahashi